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Role of Gas-Phase Halogen Bonding in Ambient Chemical Ionization Mass Spectrometry Utilizing Iodine

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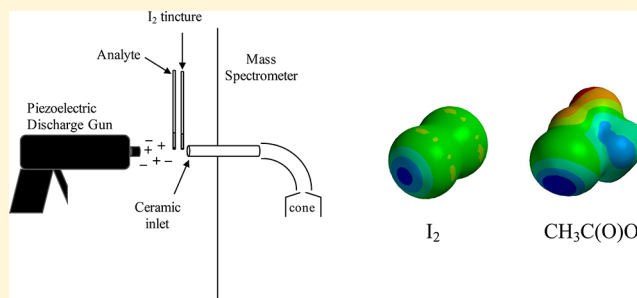
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Supporting Information

ABSTRACT: Ambient ionization processes are becoming more widely used for the measurement of atmospherically relevant particles and gases. We report here ambient ionization mass spectra utilizing a commercial tincture of iodine and a piezoelectric discharge gun (PDG) to generate the ionizing reagents. Analytes include Cl_2 , Br_2 , HNO_3 , the C_1 – C_9 series of saturated monocarboxylic acids, benzoic acid, 2,2-dimethylpropanoic acid, 9-decenoic acid, and trichloroacetic acid. While Cl_2 and Br_2 form the $[\text{M} + \text{I}]^-$ iodide adducts, HNO_3 and the organic acids show unexpected peaks corresponding to $[\text{2M} - 2\text{H} + \text{I}]^-$. For HNO_3 , the new ion formed is interpreted as the $[\text{NO}_3 \cdots \text{IONO}_2]$ complex, where IONO_2 is likely formed upon reaction of HOI with gaseous NO_3^- . Similarly, for the organic acids, the $[\text{2M} - 2\text{H} + \text{I}]^-$ peaks are interpreted as $[\text{RC}(\text{O})\text{O}^- \cdots \text{IOC}(\text{O})\text{R}]$ complexes formed by association of $\text{RC}(\text{O})\text{O}^-$ with acyl hypoiodites $[\text{RC}(\text{O})\text{OI}]$. It is proposed that the association of (1) Cl_2 and Br_2 with I^- , (2) IONO_2 with NO_3^- ions, and (3) $\text{RC}(\text{O})\text{OI}$ with carboxylate ions occurs via non-covalent halogen bonding. The results suggest the possibility that halogen bonding may play a role in chemical transformations in the atmosphere, particularly in particles where concentrations of iodinated species may be significant.

KEYWORDS: halogen bonding, ambient ionization, plasma discharge gun, iodine, chemical ionization mass spectrometry, acyl hypoiodite



INTRODUCTION

An extensive set of ion–molecule reactions forms the basis for ionization prior to mass spectrometry detection of atmospherically relevant species. One approach relies on a single ion attaching to an analyte gas [chemical ionization mass spectrometry (CIMS)],^{1–7} while another uses a series of more complex ion–molecule reactions [e.g., atmospheric pressure chemical ionization (APCI), and ambient ionization mass spectrometry]. In the first case, chemical ionization reagents, such as ethanol and/or acetone, have been used for the detection of atmospheric amines and amides,^{8–10} nitrate ions for detection of sulfuric acid^{11,12} and highly oxygenated molecules (HOMs),^{13,14} CF_3O^- ions for the detection of hydroperoxides¹⁵ and organic nitrates,¹⁶ SF_6^- ions for the detection of nitric acid and SO_2 ^{17,18} as well as organic acids,¹⁹ acetate ions for the detection of inorganic and organic acids,^{20–22} and Cl_3^- and SiF_5^- for the detection of nitric acid.^{23,24} Most relevant to the current work is iodide chemical ionization mass spectrometry (I^- CIMS), where the analyte M clusters with iodide ions to form $[\text{M} + \text{I}]^-$ adducts.^{18,25–32} This technique has been used to measure halogen compounds in air^{30,32–40} as well as many other inorganic and organic compounds.^{1,18,29,31,35,41–47}

A number of emerging methods that fall into the ambient ionization category^{3,48–52} are seeing increased use in the field

of atmospheric chemistry. Among these are direct analysis in real time mass spectrometry (DART–MS), extractive electrospray ionization mass spectrometry (EESI–MS), and easy ambient sonic spray ionization mass spectrometry (EASI–MS). The advantage of these methods is being able to analyze a variety of samples without the need for collection or sample workup, such as particles on the fly^{53–59} and gases.^{60–66} Because the ionization is generally carried out at atmospheric pressure in room air, other trace species in addition to the analyte are ionized concomitantly. If these species occur in a high enough concentration, they may alter the ionization of the analyte,⁶⁰ but with care, these complications can be minimized and taken into account.

Some of these ambient methods rely on plasmas to generate the ionization agents.^{2,51,52,67–70} One such plasma source utilizes a piezoelectric discharge, which has been used to vaporize and ionize analytes in a stream of liquid solvent⁷¹ and to identify gaseous contaminants in room air.⁶⁰ Piezoelectric discharge guns (PDGs) are inexpensive and widely available because they are used to remove static charges from surfaces.

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The PDG generates a pulse of both positive ions (trigger compression) and negative ions (trigger release) in a single manual “squeeze and release” cycle via mechanical distortion of a piezoelectric element. Previous studies have shown that ionization using piezoelectric devices results in soft ionization similar to DART or APCI, typically involving the addition of a proton from protonated water clusters or removal of a proton by O_2^- .^{60,71,72}

We report here studies of PDG ionization of an I_2 tincture to detect Cl_2 , Br_2 , HNO_3 , and a series of organic acids. These analytes are atmospherically significant in different ways. The halogens are important in the atmospheric oxidant cycle^{73–78} because they photolyze to form highly reactive chlorine or bromine atoms, leading to ozone formation or destruction, respectively. Nitric acid is important as a temporary reservoir to tie up highly reactive oxides of nitrogen in air, which would otherwise lead to the formation of ozone and other manifestations of photochemical air pollution.⁷⁹ Organic acids are commonly found in particles in air, arising from direct emissions and as products of oxidation of volatile organic compounds.^{80–82}

We show that, while iodide adducts (i.e., $[\text{M} + \text{I}]^-$ ions) are formed with the halogens as observed previously in CIMS studies,^{30,33–40} organic acids are detected via a different ionization chemistry. In both cases, the adducts observed demonstrate a role for halogen bonding in the gas phase. Halogen bonding is a non-covalent interaction between a positively polarized region of a halogen atom in a molecule and a nucleophilic region of a molecule (or anion).^{83,84} For example, molecular iodine shows an anisotropic electron density, with regions of negative potential on the equatorial sides on the halogen atoms and positive electrostatic potentials at the ends of the bond axis to form what is called a sigma (σ) hole^{83–91} (Figure 1) that halogen bonds to nucleophiles.

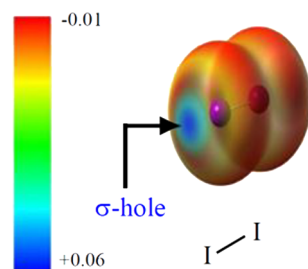


Figure 1. Electrostatic potential diagram showing a region of positive electrostatic potential, the σ hole, in molecular iodine. This figure was adapted with permission from ref 91. Copyright 2018 John Wiley & Sons, Inc.

Conceptually similar to a hydrogen bond, halogen bonding has been widely observed in many different contexts, including molecular self-assembly, drug design, organic synthesis, and biomolecular systems.^{83,87,92,93} Here, we suggest that the halogen bonding phenomenon plays an important role in the analyte clusters formed when PDG ionization of iodine tincture serves as the reagent source. Possible implications for a role of halogen bonding in atmospheric systems are discussed.

EXPERIMENTAL SECTION

Chemical Ionization by PDG Plasma. A hand-held PDG (Milty Zerostat 3 antistatic gun, Armour Home, Bishops

Stortford, U.K.) was used as an open-air ionization source at the inlet of a mass spectrometer (Figure 2). The negative ion trigger release was used to ionize samples at the tip of two open capillaries held in air about 1 mm from the inlet of the mass spectrometer. The capillaries were microhematocrit tubes coated with ammonium heparin (VWR), for which the coating was removed by sonication in nanopure water (18 M Ω cm, Thermo Scientific, Barnstead), and the capillaries dried before use. Uncoated melting point capillaries were used with similar results. The capillaries were situated perpendicularly to the inlet of a triple quadrupole mass spectrometer (Xevo TQ-S, Waters, Milford, MA, U.S.A.) operated in negative ion mode. One capillary contained the I_2 tincture, while the second contained the analyte. A selected number of experiments were also performed using methyl iodide (CH_3I), instead of the I_2 tincture as the reagent. For all experiments, a DART–MS ionization source (IonSense) equipped with the Vapur interface and a 6 cm long ceramic tube (inner diameter of 4.75 mm) was used as the MS inlet interface. The PDG replaced the helium DART probe as the ionization source, and the two capillary tubes were located in between the PDG source and the inlet of the mass spectrometer. Mass spectra were collected in negative ion mode from either a single discharge of the PDG or averaged over 2–8 slow trigger releases and analyzed using MassLynx software. For comparison, some spectra were collected with the DART–MS probe located 4 cm away from the MS inlet. DART was operated with helium reagent gas at a flow of 3.1 L min^{−1}, a He gas temperature of 150 °C, and a grid electrode voltage of −350 V in the negative ion mode.

For both methods, specific in-source parameters were as follows: cone voltage, 30 V; source offset, 50 V; no cone gas; and ion block temperature, 110 °C. These are the values set in the MassLynx software and are not absolute values with respect to ground. The inside of the ceramic tube as well as the Vapur interface were at atmospheric pressure, while the pressure behind the 0.8 mm sample cone controlled by a rough pump (i.e., ion block and T-wave region as illustrated in Figure 2) was ~ 2 mbar. The pressure in the ion guide region was maintained at $(7\text{--}8) \times 10^{-3}$ mbar, while the analyzer was operated at 1×10^{-5} mbar. Full mass spectra were acquired over 0.1 or 1 s using the second quadrupole, while the first quadrupole and collision cell acted as additional ion guides (no scanning or fragmenting). Similar spectra resulted when spectra were acquired over 0.1, 0.25, or 1 s, with improved time resolution and sensitivity obtained at faster scan rates. Improved time response was due to the better synchronization between ion bursts accompanying trigger release and MS collection with faster scan rates (see Figure S1 of the Supporting Information). The collision cell energy was typically set to 2 eV for full mass spectra, with some spectra collected using 15 eV as discussed in the Supporting Information. In separate experiments, MS/MS scans were acquired with various collision energies (2–30 eV) applied to the collision cell to investigate the fragmentation of a given species. Argon gas flow in the collision cell was maintained at 0.15 mL min^{−1} in both full MS scan and MS/MS scans.

Because static electricity removal devices are known to generate ozone as a result of the high voltages produced (3–8 kV), ozone concentrations after repeated gun squeeze/release cycles were measured using a photometric ozone analyzer (model 400E, Teledyne API) at approximately the same

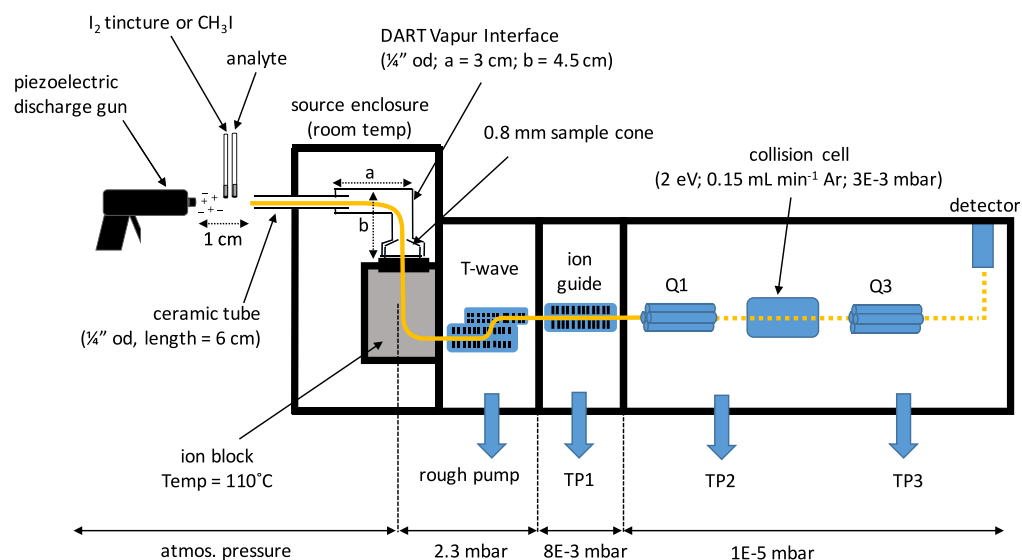


Figure 2. Schematic diagram of the mass spectrometer and source region including the placement of the PDG and sample capillaries.

distance as that between the PDG and the mass spectrometer inlet in the experiments.

Chemicals and Reagents. Iodine tincture solutions containing approximately 2% (w/w) I_2 and 2% (w/w) NaI in aqueous ethanol were obtained commercially (Walgreens) or prepared in the laboratory. In the latter case, the solution was allowed to equilibrate for several hours to establish iodide ion equilibria (*vide infra*). Iodine (>99.8%, ACS grade, Fisher Chemical), sodium iodide ($\geq 99.5\%$, EMD), and ethanol (200 proof, Goldshield Chemical Company) were used as received. Methyl iodide was purchased from Sigma-Aldrich (99%).

All acids were used as received: nitric acid (69% certified ACS plus, Fisher), formic acid (88%, Fisher), acetic acid (glacial 99.7%+, EMD), propanoic acid (99%+, Mallinckrodt), butanoic acid (99.5%, anhydrous, Sigma), pentanoic acid (99%+, Sigma-Aldrich), hexanoic acid (99.5%+, Sigma-Aldrich), heptanoic acid (99%+, Sigma-Aldrich), octanoic acid (99%, Sigma-Aldrich), nonanoic acid (96%, Sigma-Aldrich), 2,2-dimethylpropanoic (99%, Sigma-Aldrich), benzoic acid (99.5%, Sigma-Aldrich), 9-decenoic acid (95%+, Narchem), and trichloroacetic acid (99%+, Sigma-Aldrich). Liquid bromine (99.5%, ACS reagent grade) was purchased from Sigma-Aldrich, and a standard gas mixture of Cl_2 [10.58 ppm of Cl_2 ($\pm 5\%$) in N_2 , AirGas Specialty Gases] was also used.

RESULTS AND DISCUSSION

Negative Ion Mass Spectra in the Absence of Analytes. Figure 3a shows the negative ion mode mass spectrum generated by PDG ionization in laboratory air with no iodine reagents present. The inset in Figure 3a shows the total ion count as a function of time during PDG trigger release, demonstrating both the variability and signal-to-noise ratios of the method. Ions are formed and detected only during each PDG trigger release with no background ion signal between these bursts, resulting in very high signal-to-noise ratios. The ions observed are those that have been previously identified in DART and APCI as, e.g., CO_3^- (m/z 60), HCO_3^- (m/z 61), and NO_3^- (m/z 62).^{94–97} Lactic acid from human skin vapor gives rise to a peak at m/z 89 [$CH_3CH(OH)CO_2^-$].⁹⁸ The ionization mechanism that occurs for PDG

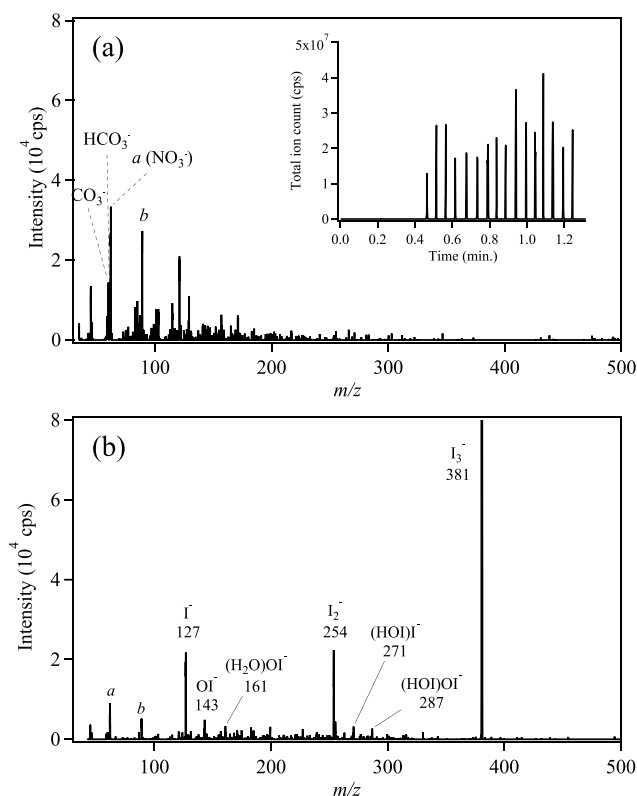


Figure 3. Mass spectra of reagent ions generated by PDG ionization of (a) laboratory air (no reagent) and (b) a commercial iodine tincture. Peaks labeled *a* and *b* at m/z 62 and 89, respectively, are due to NO_3^- and lactic acid [$M - H$] $^-$ ion, commonly observed in ambient negative ion mode spectra.^{94–97} The inset in part a shows the time resolution and reproducibility of PDG total ion counts during several squeezes.

ionization in ambient air (with no added ionization reagent) is shown in Figure S2a of the Supporting Information.

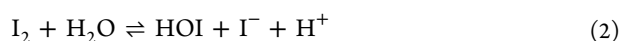
Figure 3b shows a typical negative ion mass spectrum of reagent ions generated by applying the PDG source to a commercial iodine tincture. Dominating the spectrum in Figure 3b are peaks at m/z 127 (I^-), 254 (I_2^-), and 381 (I_3^-),

along with smaller but still significant peaks at m/z 143 (OI^-), 161 ($(\text{H}_2\text{O})\text{OI}^-$), 271 ($(\text{HOI})\text{I}^-$), and 287 ($(\text{HOI})\text{OI}^-$). A detailed ionization mechanism for the ions observed is illustrated in Figure S2b of the Supporting Information. A small peak IO_3^- (175) was also observed in many cases.

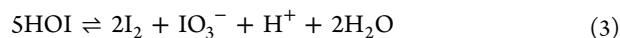
The multiplicity of iodine-containing reagent ions in Figure 3b arises in part from a series of complex equilibria common to aqueous iodine solutions.^{99,100} Commercial iodine tinctures used as skin disinfectants contain 2% I_2 in water as well as 2% NaI or KI and ethanol to aid in the dissolution of I_2 . An equilibrium between molecular iodine, iodide, and triiodide is established over several hours in the tincture solution (reaction 1).



Molecular iodine hydrolyzes in water to form hypiodous acid (HOI),¹⁰¹



which readily disproportionates, forming the iodate ion, IO_3^- , and regenerating iodine.



Hypiodous acid is able to partition from aqueous solution to the gas phase [$K_{\text{H}} = (2-5) \times 10^{-3} \text{ atm M}^{-1}$],^{102,103} although less readily than molecular iodine ($K_{\text{H}} = 0.3 \text{ atm M}^{-1}$).¹⁰³ Laboratory-prepared solutions containing either molecular iodine or an iodide salt, but not both, did not generate the abundance of iodide reagent ions that the I_2/I^- tincture provided upon ionization. Thus, both I_2 and I^- are important species, suggesting the equilibria in reactions 1–3 are responsible for the generation of reagent ions in these experiments. Supporting these equilibria in the liquid tincture, ultraviolet (UV)-visible measurements of the tincture showed the presence of I_2 , I_3^- , and HOI (Figure S3 of the Supporting Information).

The observed iodine species were investigated by collecting full MS scans of the I_2 tincture using PDG and DART-MS ionization at low and high collision cell energies. Panels a and b of Figure S4 of the Supporting Information show that PDG ionization at a collision cell energy of 2 eV yields ion adducts of HOI and OI^- at m/z 161 ($(\text{H}_2\text{O})\text{OI}^-$), 271 ($(\text{HOI})\text{I}^-$), and 287 ($(\text{HOI})\text{OI}^-$) (the same as Figure 3b), while a higher collision cell energy of 15 eV leads to their fragmentation. The ions I^- , OI^- , I_2^- , and I_3^- remain dominant at both collision energies. For comparison, DART-MS, which is known to generate O_2^- ,⁹⁶ was used to collect negative ion mode spectra of the I_2 tincture. Panels c and d of Figure S4 of the Supporting Information show DART-MS spectra using collision cell energies of 2 and 15 eV, respectively. A comparison of DART and PDG ionization at 2 eV shows that the ions generated from the I_2 tincture for both methods of ionization include dominant I^- , I_2^- , and I_3^- ions and small contributions from OI^- and HOI ion adducts. Similarly, the spectra using PDG and DART at a collision cell energy of 15 eV are comparable, in which I^- , I_2^- , and I_3^- remain the major ions, while the HOI and OI^- adducts are fragmented. These data show that the mechanism of ionization provided by piezoelectric ionization in ambient air is analogous to that provided by ionization using DART-MS.⁹⁶ The identification of ions at m/z 143 (OI^-), 161 ($(\text{H}_2\text{O})\text{OI}^-$), 271 ($(\text{HOI})\text{I}^-$), and 287 ($(\text{HOI})\text{OI}^-$) was

confirmed with product ion scans carried out with DART-MS (Figure S5 of the Supporting Information).

While there is considerable variability in the total ion counts of the iodine adducts using PDG from pulse to pulse (inset in Figure 3a), I^- and I_3^- consistently comprise the largest percentage of ion counts in PDG ionization of iodine tincture. The reproducibility of the charge generated during successive squeezes of the PDG is unknown and may contribute to this variability, as could oxidation chemistry in the ionization region involving oxygen and/or ozone. Although a maximum of 607 ppb of O_3 was generated by 30 successive trigger squeeze/release cycles, ozone formation was minimized in experiments reported here using either a single trigger release or an average over 2–8 trigger releases. However, secondary chemistry between ozone and iodide ions may still occur, causing the additional formation of oxyanions and perturbing the equilibria shown in reactions 1–3. Ozone is known to react with aqueous iodide at the air–water interface to generate iodine oxyanions.^{104–106} The exposure of aqueous NaI solutions to a flow of ozone at levels above 50 ppb was shown previously to generate oxidized forms of iodine detected by electrospray ionization mass spectrometry (ESI-MS), including OI^- , IO_2^- , and IO_3^- .¹⁰⁵

To investigate the effect of O_3 on the distribution of ions, a slow flow of several parts per million (ppm) of O_3 , generated from 185 nm photolysis of O_2 , was introduced during ionization. The peak at m/z 175 (IO_3^-) increased significantly, consistent with known O_3 –iodide chemistry. Other oxyanions were not observed. The peak intensities of OI^- , I^- , and I_3^- did not change significantly when several ppm O_3 were present.

For comparison to traditional I^- CIMS studies, in which the ionizing reagent is often formed under slight vacuum and in an inert N_2 atmosphere, PDG ionization of CH_3I was carried out. The major ions observed were I^- with some IO_3^- (Figure S6a of the Supporting Information). It is important for the later discussion to note that there is no OI^- peak at m/z 143 or HOI adducts observed using CH_3I as the precursor. Iodide ion (I^-), its clusters with water, and I_3^- have been reported in I^- CIMS studies employing ionization of CH_3I with discharge processes,³² X-ray,^{107,108} or radioactive sources, such as ^{210}Po .^{26,30,33,38,40,109,110} In the case of I^- CIMS using ^{210}Po for example, I^- is generated via dissociative electron attachment to CH_3I . Lee et al.³⁰ reported the presence of minor ions, such as OI^- , IO_2^- , and IO_3^- , from CH_3I ionization with a ^{210}Po source, and other discharge sources using CH_3I have been reported to generate not only IO_3^- but also OI^- , IO_2^- , and IO_4^- .³² In electrospray chemical ionization techniques using iodide salt solutions as the reagent ionization source, only I^- and I_3^- are observed.^{111,112}

Application to Cl_2 and Br_2 . As proof of concept, the PDG ionization technique using the iodine tincture reagent source was applied to gaseous Cl_2 and liquid Br_2 . Mass spectra are shown in Figure 4. As expected, both Br_2 and Cl_2 form iodide adducts. This result is not surprising, because Lee et al.³⁵ reported Cl_2I^- and Br_2I^- clusters from I^- CIMS measurements using CH_3I and suggested that their high polarizabilities (31.36 bohr³ and 46.72 bohr³, respectively) contribute to their strong cluster formation. Thus, peaks as a result of Cl_2I^- are found at m/z 197, 199, and 201, and peaks as a result of Br_2I^- are found at m/z 285, 287, and 289, with the ratios of the peak intensities in both cases as expected from the isotopic abundances of chlorine and bromine.

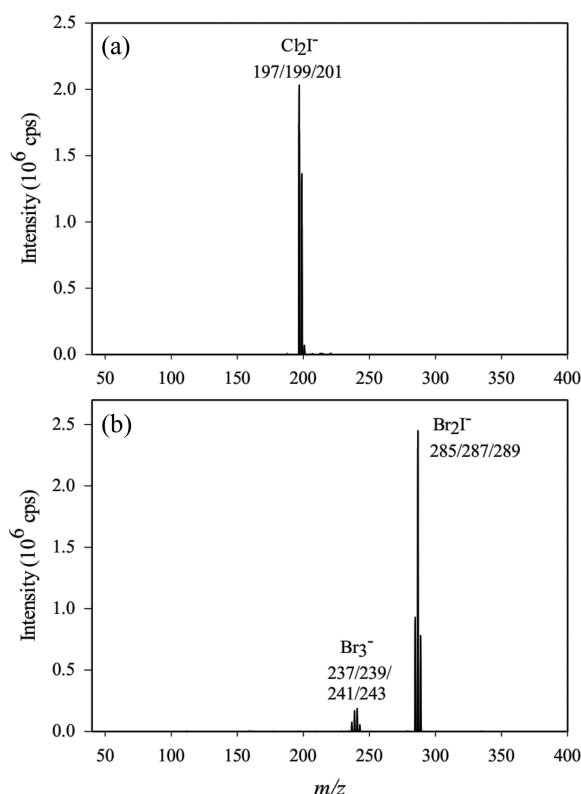


Figure 4. Mass spectrum of (a) gas-phase chlorine and (b) liquid bromine ionized by PDG with the iodine tincture.

The detection of the gaseous trihalide ion adducts I_3^- , Cl_2I^- , Br_2I^- , and Br_3^- (Figures 3b and 4) illustrates the unusual stability of the halogen bond in these adducts. Anionic halogen bond acceptors are generally stronger than neutral species, and the strength of the halogen donor increases in the order $Cl < Br < I$. Solution-phase triiodide ion is a hallmark example of a halogen bond occurring through a σ hole on molecular iodine interacting with the iodide anion through the $I_2 \cdots I^-$ association (180 kJ/mol).^{87,89} We assert that this same interaction in the gas phase accounts for the presence of I_3^- , Cl_2I^- , Br_2I^- , and Br_3^- reported here.

Application to Nitric Acid. Figure 5 presents the mass spectrum observed when the headspace of a 15.8 M HNO_3 solution is analyzed using PDG ionization of the I_2 tincture.

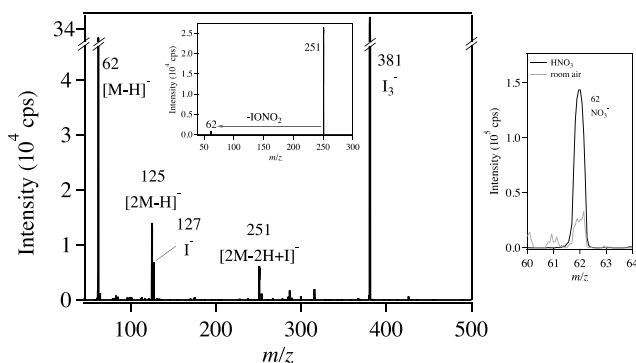


Figure 5. Mass spectrum of PDG-ionized HNO_3 with the iodine tincture. The inset is the product ion scan of m/z 251 acquired at a collision cell energy of 5 eV. For comparison, background NO_3^- ion intensity is shown on the right.

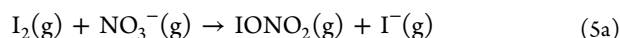
Peaks appear at m/z 62 (NO_3^- , with intensities 5–10 times above background NO_3^- levels) and m/z 125 (corresponding to the $[2M - H]^-$ adduct). These ions, $[M - H]^-$ and $[2M - H]^-$, are expected on the basis of traditional APCI mechanisms. Under the ambient ionization conditions and the high concentrations of HNO_3 used here, the dimer ion is observed. In contrast to the halogens, no $[M + I]^-$ adduct is observed, despite the high binding energy of HNO_3 with I^- .^{29,44} However, an unexpected iodide cluster is observed at m/z 251, corresponding to $[2M - 2H + I]^-$.

Product ion scans were performed to examine the fragmentation pattern of the $[2M - 2H + I]^-$ cluster. Using collision energies ranging from 2 to 30 eV, the product ion spectra showed that the cluster at m/z 251 dissociates to NO_3^- , with a neutral loss of iodine nitrate, $IONO_2$ (inset in Figure 5). This is consistent with the formation of $[2M - 2H + I]^-$ via the reaction of NO_3^- with $IONO_2$.



Higher collision energies did not induce further fragmentation of $IONO_2$.

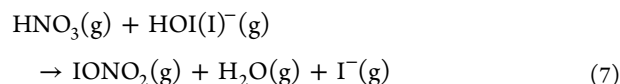
The presence of a σ hole on the iodine atoms of I_2 and HOI is known to promote halogen bonding,^{113–116} likely with the NO_3^- anion. In this vein, we propose that $IONO_2$ is formed in the gas phase via reactions 5a and 5b.



Supporting I_2 and HOI in the ionization region is the observation in mass spectra (Figure 3b) of I_2^- , OI^- , $(H_2O)OI^-$, $(HOI)I^-$, and $(HOI)OI^-$. The ion OI^- is likely from the deprotonation of HOI . There are other ion–molecule reactions that are possible, which include the reaction of OI^- with nitric acid (reaction 6).



However, on the basis of thermodynamics (Table S1 of the Supporting Information), OI^- is expected to deprotonate HNO_3 in competition with the potential chemistry in reaction 6). Another possibility is the reaction of HOI ion clusters, such as $HOI(I)^-$, with HNO_3 (reaction 7).



However, the intensities of the HOI clusters are relatively small compared to the NO_3^- peak intensity, suggesting that this is less important. The absence of a $[M + I]^-$ adduct upon HNO_3 analysis with the I_2 tincture suggests that HNO_3 is deprotonated to form NO_3^- upon PDG ionization. Because ambient ionization methods commonly generate O_2^- ions, as in DART and APCI,^{95,96} deprotonation of HNO_3 by O_2^- must dominate over adduct formation between HNO_3 and I^- under these ambient conditions. Thus, acids more acidic than HO_2 in the gas phase will be deprotonated by O_2^- , and their anions will be observed in the spectrum (see Table S1 of the Supporting Information).

DART–MS spectra of I_2 tincture in the absence and presence of nitric acid were collected for comparison. Figure S7 of the Supporting Information shows that, when HNO_3 is present, the HOI/OI^- adducts are not observed and peaks at m/z 62, 125, and 251 appear in similar relative ratios observed

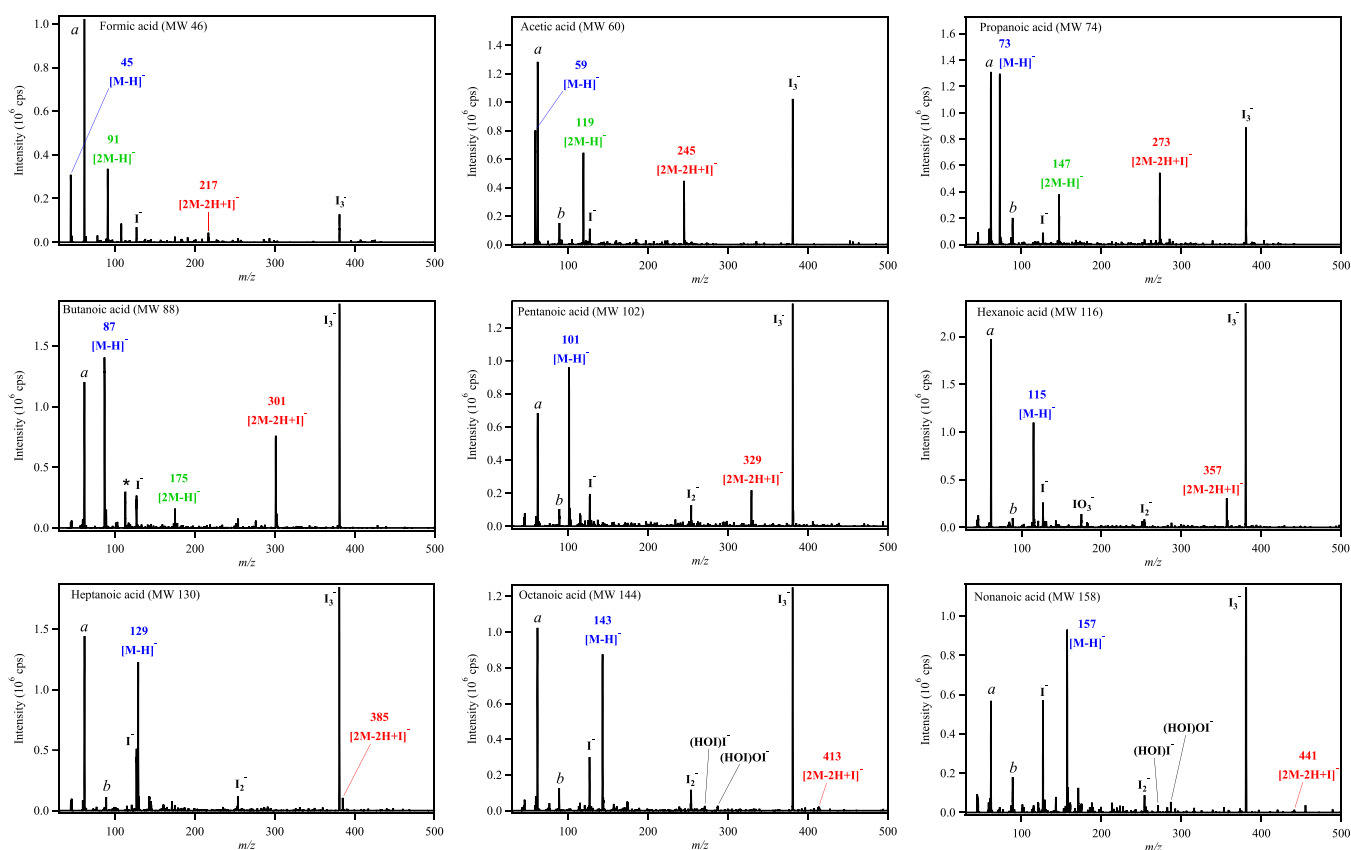


Figure 6. Mass spectra of C_1 – C_9 alkanolic acids ionized by PDG with the iodine tincture showing locations of $[M - H]^-$ (blue), $[2M - H]^-$ (green), and $[2M - 2H + I]^-$ (red). The $[2M - H]^-$ adducts for C_5 – C_9 are present in each spectrum but too small to be seen with the displayed scale. The I_3^- peak is off scale in some spectra. Peaks labeled *a* and *b* at m/z 62 and 89, respectively, are due to NO_3^- and lactic acid $[M - H]^-$. A contaminant peak (labeled with an asterisk) was observed at m/z 113 for butanoic acid.

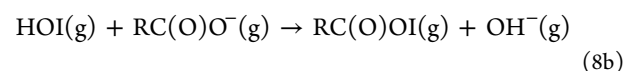
for PDG ionization (Figure 5). This supports that PDG and DART generate the deprotonating agent, O_2^- , with similar mechanisms and that NO_3^- forms an adduct with both $IONO_2$ to form the $[2M - 2H + I]^-$ cluster and HNO_3 to yield the dimer ion, $[2M - H]^-$.

Application to Monocarboxylic Acids. To assess the ability of PDG-generated ions from the iodine tincture to detect organic acids, a homologous series of monocarboxylic acids (C_1 – C_9 alkanolic acids) was investigated. Mass spectra resulting from the simultaneous ionization of each of the C_1 – C_9 monocarboxylic acids with the iodine tincture at the mass spectrometer inlet are presented in Figure 6. Spectra are dominated by the $[M - H]^-$ ion (blue labels in Figure 6). This is in contrast to reported I^- CIMS using CH_3I and a ^{210}Po source, where very small carboxylate signals were observed relative to $[M + I]^-$.³⁰ Peaks corresponding to $[2M - H]^-$ ions (green labels in Figure 6) were also clearly observed for the C_1 – C_4 acids. For the $\geq C_5$ acids, the $[2M - H]^-$ ion peaks were very small. However, an unexpected iodide cluster corresponding to $[2M - 2H + I]^-$, appears in the mass spectra of all of the C_1 – C_9 acids (red labels in Figure 6) at m/z 217 (C_1), 245 (C_2), 273 (C_3), 301 (C_4), 329 (C_5), 357 (C_6), 385 (C_7), 413 (C_8), and 441 (C_9).

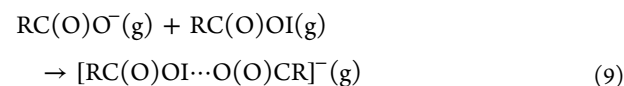
Product ion scans were again performed to examine the fragmentation patterns of the $[2M - 2H + I]^-$ cluster. Scans were recorded at increasing collision energies ranging from 2 to 30 eV. The product ion spectra of each of the $[2M - 2H + I]^-$ ions for the homologous series showed the corresponding $[M - H]^-$ ion (see two representative MS/MS spectra for

acetic and nonanoic acids in Figure S8 of the Supporting Information). From those, a neutral loss of $[M - H + I]$ is observed for all acids and is consistent with the homologous series of the acyl hypoiodites, $RC(O)OI$.

Acyl hypoiodites are generally regarded as transient species in solution-phase iodination chemistry.^{117–119} However, acetyl hypoiodite has recently been detected by gas chromatography–mass spectrometry (GC–MS) in an acetic acid solution containing iodine and *t*-butyl hydroperoxide,⁹¹ and Urbansky et al. postulated the formation of acetyl hypoiodite in solutions of acetic acid, acetate ion, and hypoiodous acid.¹²⁰ By analogy to the HNO_3 observations presented above (reactions 5a and 5b), we propose that acyl hypoiodites are formed in the gas phase through the reactions 8a and 8b of I_2 or HOI with $RC(O)O^-$.



$RC(O)O^-$ is generated by the reaction of $RCOOH$ with O_2^- (Figure S2 of the Supporting Information) upon PDG ionization and is proposed to react with $RC(O)OI$ to form the $[2M - 2H + I]^-$ adduct in the gas phase via reaction 9.



The apparent stability of these unusual $[2M - 2H + I]^-$ clusters may be reconciled through halogen bonds. Acyl hypoiodites are known to possess a larger σ hole on the extension of the O–I axis, as shown in Figure 7, than

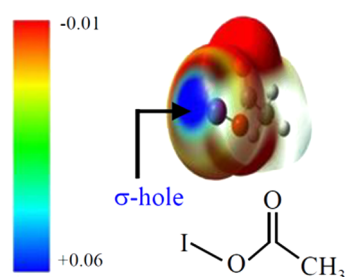


Figure 7. Electrostatic potential diagram showing the σ hole in acetyl hypoiodite on the same scale as Figure 1. This figure was adapted with permission from ref 91. Copyright 2018 John Wiley & Sons, Inc.

molecular iodine has on the extension of the I–I axis (Figure 1).⁹¹ The strength of the halogen bond interaction increases with the size of the σ hole. We propose that an attractive non-covalent interaction between the electrophilic region of the iodine atom in $RC(O)OI$ and the nucleophilic carboxylate anion, $RC(O)O^-$, the Lewis base, may account for the $[2M - 2H + I]^-$ clusters.

Further evidence that reactions 8 and 9 occur in the gas phase is provided by experiments in which the C_5 and C_6 acid liquids were held in two separate capillaries and ionized alongside the capillary containing iodine tincture with the PDG. Mass spectra from this experiment show the C_5 $[2M_5 - 2H + I]^-$ cluster, the C_6 $[2M_6 - 2H + I]^-$ cluster, and a mixed C_5/C_6 $[M_5 + M_6 - 2H + I]^-$ cluster, as shown in Figure 8.

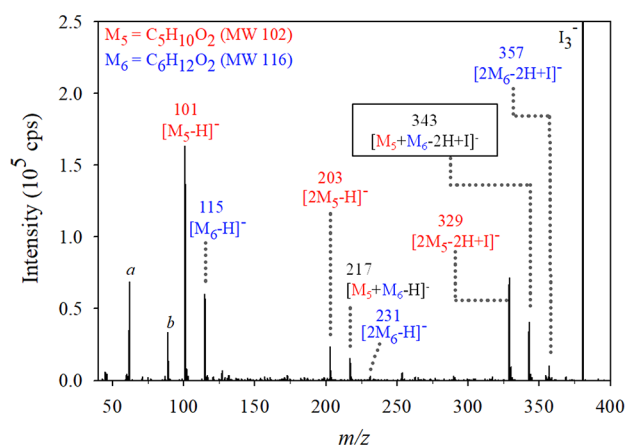


Figure 8. Mass spectrum obtained from PDG ionization of the iodine tincture and pentanoic and hexanoic acids each in separate capillaries showing the formation of a mixed C_5/C_6 $[M_5 + M_6 - 2H + I]^-$ cluster at m/z 343. Peaks labeled *a* and *b* at m/z 62 and 89, respectively, are due to NO_3^- and lactic acid $[M - H]^-$.

Because the liquid analytes are in separate capillaries and are not in contact with each other, a mixed cluster can only form if the C_5 and C_6 acids evaporate before they are ionized by PDG. The presence of the mixed C_5/C_6 cluster upon ionization of each acid held in separate capillaries therefore confirms that the $[2M - 2H + I]^-$ ions form in the vapor phase. As seen in Figure 9, MS/MS experiments again show the expected

product ions $[M - H]^-$ for C_5 and C_6 acids, which correspond to the neutral loss of $RC(O)OI$.

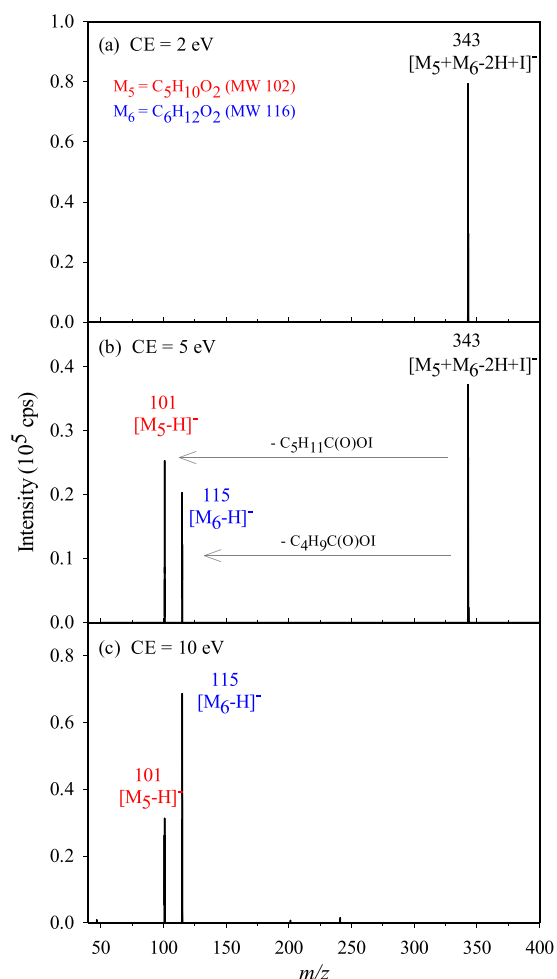
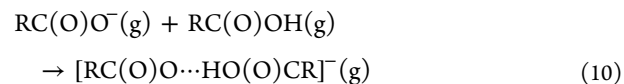


Figure 9. Product ion scans of the m/z 343 $[M_5 + M_6 - 2H + I]^-$ cluster identified in Figure 8 at collision energies of (a) 2 eV, (b) 5 eV, and (c) 10 eV.

A competitive interaction will exist between hydrogen bond and halogen bond formation in the detected $[2M - H]^-$ and $[2M - 2H + I]^-$ adducts. Thus, in competition with reaction 9, $RC(O)O^-$ may come into contact with undissociated $RCOOH$ molecules in the vapor phase, leading to $[2M - H]^-$ adducts (reaction 10).



For both formic and acetic acids, the $[2M - H]^-$ ion is more intense than the $[2M - 2H + I]^-$ cluster (Figure 6). As the carbon chain length increases, there is a preference to form halogen-bonded $[2M - 2H + I]^-$ over the hydrogen-bonded adduct, $[2M - H]^-$. This trend is shown in Figure 10, in which the $[2M - H]^-/[2M - 2H + I]^-$ peak intensity ratio is provided for each of the C_1 – C_9 monocarboxylic acids. The stability of the longer chain clusters $[2M - 2H + I]^-$ may be due to a larger number of accessible vibrational modes, which allow excess energy to be redistributed.

As the carbon chain lengthens in the homologous acid series, the positive inductive effect of the aliphatic chain of the acyl

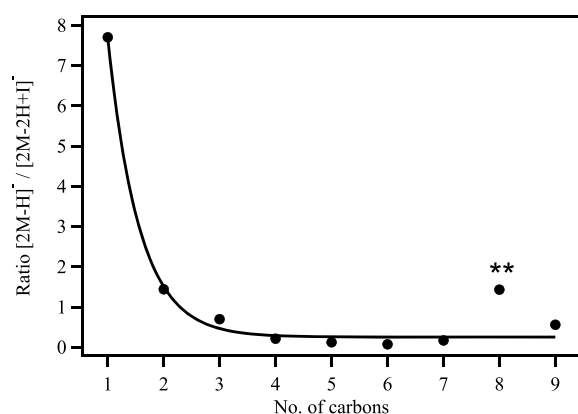


Figure 10. Ratio of $[2M-H]^-$ to $[2M-2H+I]^-$ peak intensities for C_1 – C_9 alkanolic acids ionized by PDG with the iodine tincture. The curve is a guide for the eye only. The presence of $(HOI)OI^-$ ion at m/z 287 (**) interferes with the $[2M-H]^-$ ion for C_8 .

hypoiodite is expected to increase. Although it would seem that this would reduce the electrophilicity of the iodine atom, thereby decreasing the size of the σ hole, instead, the longer chains appear to stabilize the halogen bond. This counter-intuitive trend was noted in a density functional theory (DFT) study of C_1 – C_5 acyl hypoiodites interacting with substituted pyridine bases⁹¹ and other halogen bond studies.^{121,122} Guha and Sekar⁹¹ report that the increasing positive inductive effect across the acyl hypoiodite series lowers the lowest unoccupied molecular orbital (LUMO) acceptor orbital energies relative to the energy of the highest occupied molecular orbital (HOMO)

donor orbital, resulting in a significant mixing of the frontier orbitals. In addition, the nucleophilicity of $RCOO^-$ increases as its carbon chain lengthens, increasing its attraction to the σ hole. Thus, increasing the carbon chain length on both reactants in reaction 9 acts to stabilize $[2M-2H+I]^-$ adduct formation.

To gain further insight into the formation mechanism for $[2M-2H+I]^-$ clusters, each of the acids were ionized with the PDG ionization technique using CH_3I as the reagent ion source instead of the I_2 tincture. None of the acids formed the $[2M-2H+I]^-$ clusters, and only the $[M-H]^-$ ion was consistently observed. Examples are shown in panels b–d of Figure S6 of the Supporting Information for acetic, hexanoic, and octanoic acids. This result lends strong support for reactions of HOI and its clusters with $RCOO^-$ as the origin of acyl hypoiodite in the I_2 tincture spectra.

Applications to Other Carboxylic Acids. Carboxylic acids having structural features not found in the alkanolic acid series were studied to ascertain whether the $[2M-2H+I]^-$ cluster would form. Specifically, benzoic acid (Figure 11a), observed in indoor air,¹²³ and 2,2-dimethylpropanoic acid (Figure 11b), emitted from building materials,^{124,125} both formed the $[2M-2H+I]^-$ cluster. In addition, a monounsaturated acid, 9-decenoic acid, found in the head-space of wine¹²⁶ and other foods^{127–132} also forms the $[2M-2H+I]^-$ cluster (Figure 11c). These data demonstrate that both alkyl and aryl carboxylic acids lead to gas-phase RCOOI formation, followed by halogen bond formation with their $RCOO^-$ counterparts. Aryl (Ar) hypoiodites are known to interact with carboxylate ions through non-covalent inter-

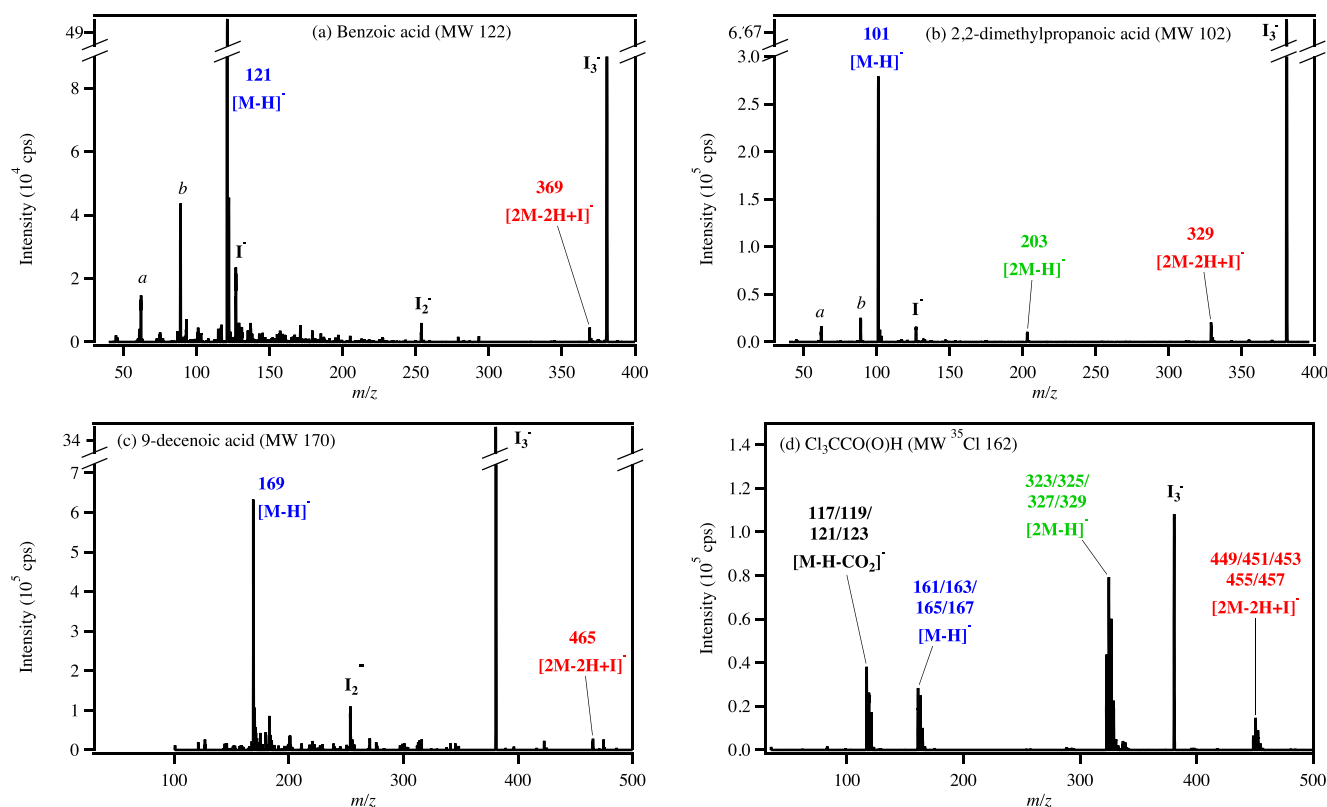


Figure 11. Mass spectra obtained from PDG ionization with the iodine tincture of (a) benzoic acid, (b) 2,2-dimethylpropanoic acid, (c) 9-decenoic acid, and (d) trichloroacetic acid. In panel d, the molecular weight of only the ^{35}Cl isotopomer is provided but the analyte contained the natural abundances of all isotopomers. Peaks labeled a and b at m/z 62 and 89, respectively, are due to NO_3^- and lactic acid $[M-H]^-$.

actions to form ions of the type $[\text{Ar}-\text{C}(\text{O})\text{OI}\cdots\text{O}(\text{O})\text{C}-\text{Ar}]^-$.¹³³

Finally, trichloroacetic acid (Figure 11d), which has been measured in air^{134,135} and water,¹³⁶ shows the $[2\text{M} - 2\text{H} + \text{I}]^-$ peak and also gives rise to a $[\text{M} - \text{H} - \text{CO}_2]^-$ peak, characteristic of trihaloacetic acids.¹³⁷ The presence of the $[2\text{M} - 2\text{H} + \text{I}]^-$ peak speaks to the negative inductive effect provided by the chlorine substituents, which render iodine in the corresponding trichloroacetyl hypoiodite more positive.^{138,139} In short, the $[2\text{M} - 2\text{H} + \text{I}]^-$ cluster forms consistently for a variety of carboxylic acids with a range of structural features.

The formation of gaseous acyl hypoiodite ion clusters, $[2\text{M} - 2\text{H} + \text{I}]^-$, is the first direct evidence for halogen bonding in plasma-induced ionization in the gas phase. Given the importance of halogen chemistry in the troposphere,^{76,78,140,141} the question arises as to whether halogen bonding may play a role in chemical processes in the atmosphere. Halogen-bonded complexes between CH_3I and CCl_4 with oxygenated organics¹⁴² have been observed, and theoretical studies of HOI binding to dimethyl sulfoxide¹¹³ and monohaloamines¹⁴³ predict halogen bonding in those cases as well. There is also evidence for halogen bonding of water with HOX (X = F, Cl, and Br)¹⁴⁴ and with CF_4 and CCl_4 .¹⁴⁵ Of these possibilities in the atmosphere, only water is likely to be present in sufficient concentrations to complex significantly in the gas phase under atmospheric conditions, potentially affecting the reactivity of the halogen compound.

However, halogen bonding may play a more important role in the condensed phase found in particles. Yu et al.¹⁴⁶ reported the presence of a number of organic iodine compounds in particles in China under conditions where new particle formation was occurring. They proposed formation via electrophilic substitutions involving I^+ formed from HOI or I_2 . However, it might be that the formation of these organoiodine compounds actually proceeds via halogen bonds rather than I^+ . Thus, the contribution of halogen bonds, especially for HOI and other iodine-containing species, warrants further investigation in the condensed-phase chemistry of the marine boundary layer.

CONCLUSION

A hand-held PDG combined with a commercial iodine tincture was shown to generate a suite of ions during ambient ionization with the detected adducts, with strong evidence for halogen bonding. The technique is shown to detect the molecular halogens, Cl_2 and Br_2 , as well as nitric and organic acids. For the acids, secondary chemistry occurs involving hypoiodite to generate $[2\text{M} - 2\text{H} + \text{I}]^-$ cluster ions, which are stabilized through halogen bonding between acyl hypoiodites and the deprotonated acids. This chemistry is analogous to the reaction of HOI with NO_3^- to form IONO_2 . The formation of $[2\text{M} - 2\text{H} + \text{I}]^-$ cluster ions is the first direct evidence for halogen bonding in the gas phase following plasma-induced ionization.

The observations of halogen bonds with the atmospherically relevant species in these studies suggest that this bonding may play a role in the troposphere. While the importance of halogen bonding in the troposphere is likely to be limited to iodine species interacting with water vapor as a result of the high concentrations of the latter, halogen bonding may be important in the condensed particle phase in which organic

iodine compounds have been implicated in new particle formation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.9b00030.

Time resolution and influence of the instrument scanning rate (Figure S1), proposed mechanisms for PDG ambient ionization (Figure S2), UV/vis spectra of liquid iodine tincture (Figure S3), negative ion mode mass spectra of I_2 tincture using PDG and DART ionization (Figure S4), product ion scans of HOI and OI^- adducts (Figure S5), mass spectra generated using PDG ionization of CH_3I with and without carboxylic reagents (Figure S6), negative ion mode DART mass spectra of I_2 tincture in the absence and presence of HNO_3 (Figure S7), product ion scans of the $[2\text{M} - 2\text{H} + \text{I}]^-$ clusters formed from PDG ionization with the I_2 tincture for acetic and nonanoic acids (Figure S8), and thermodynamic data of relevant species (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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